AFRL-RZ-WP-TP-2012-0122

SM AND ND SUBSTITUTIONS IN YBCO FILMS PRODUCED THROUGH METAL ORGANIC DEPOSITION (POSTPRINT)

B.C. Harrison, J. Carpenter, P. Klenk, and P.N. Barnes

Mechanical Energy Conversion Branch
Energy/Power/Thermal Division

H. Fang

University of Houston

C.V. Varanasi

University of Dayton Research Institute

FEBRUARY 2012

AIR FORCE RESEARCH LABORATORY
PROPULSION DIRECTORATE
WRIGHT-PATTERSON AIR FORCE BASE, OH 45433-7251
AIR FORCE MATERIEL COMMAND
UNITED STATES AIR FORCE

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YY)*	2. REPORT TYPE	3. DATES COVERED *(From - To)*
February 2012	Conference Paper Postprint	01 January 2004 – 01 January 2006

4. TITLE AND SUBTITLE
SM AND ND SUBSTITUTIONS IN YBCO FILMS PRODUCED THROUGH METAL ORGANIC DEPOSITION (POSTPRINT)

5a. CONTRACT NUMBER
In-house

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER
62203F

6. AUTHOR(S)
B.C. Harrison, J. Carpenter, P. Klenk, and P.N. Barnes (AFRL/RZPG)
H. Fang (University of Houston)
C.V. Varanasi (University of Dayton Research Institute)

5d. PROJECT NUMBER
3145

5e. TASK NUMBER
32

5f. WORK UNIT NUMBER
314532ZE

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Mechanical Energy Conversion Branch (AFRL/RZPG)
Energy/Power/Thermal Division
Air Force Research Laboratory, Propulsion Directorate
Wright-Patterson Air Force Base, OH 45433-7251
Air Force Materiel Command
United States Air Force

University of Houston
Department of Mechanical Engineering
Houston, TX 77204

University of Dayton Research Institute
300 College Park
Dayton, OH 45469

8. PERFORMING ORGANIZATION REPORT NUMBER
AFRL-RZ-WP-TP-2012-0122

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Air Force Research Laboratory
Propulsion Directorate
Wright-Patterson Air Force Base, OH 45433-7251
Air Force Materiel Command
United States Air Force

10. SPONSORING/MONITORING AGENCY ACRONYM(S)
AFRL/RZPG

11. SPONSORING/MONITORING AGENCY REPORT NUMBER(S)
AFRL-RZ-WP-TP-2012-0122

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution unlimited.

13. SUPPLEMENTARY NOTES
Conference paper published in the proceedings of the *Advances in Cryogenic Engineering: Transactions of the International Cryogenic Materials Conference*, Vol. 52, 2006. This conference was held in Keystone, CO, 29 August through 02 September 2005.

 Work on this effort was completed in 2006. This paper contains color.

PA Case Number: AFRL/WS 06-0223; Clearance Date: 06 Dec 2006.

14. ABSTRACT
Epitaxial $YBa_2Cu_3O_{7-x}$ (YBCO) films were produced on non-buffered (100) single crystal $LaAlO_3$ using the metal organic deposition (MOD) method with fluorinated metal acetates. In an effort to enhance the in-field performance of the films, Sm and Nd acetates were fractionally substituted for Y acetate in a series of precursor solutions to incorporate an array of nanoscale flux pinning centers in the post-annealed films. From measurements taken in the non-optimized films a 50%-150% improvement in critical current density at 77K in fields up to IT were found for films with a 1/3 substitution of the Rare Earth elements, with farther improvements at 40K. Furthermore, a study of the microstructure of the films by scanning electron microscopy (SEM) reveals the presence of nanoparticles on the surfaces of the films.

15. SUBJECT TERMS
non-buffered, post-annealed, non-optimized, microstructure, scanning electron microscopy, nanoscale flux pinning centers

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT:	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON (Monitor)
a. REPORT	b. ABSTRACT	c. THIS PAGE			Timothy J. Haugan
Unclassified	Unclassified	Unclassified	SAR	12	19b. TELEPHONE NUMBER *(Include Area Code)* N/A

SM AND ND SUBSTITUTIONS IN YBCO FILMS PRODUCED THROUGH METAL ORGANIC DEPOSITION

B.C. Harrison[1], H. Fang[2] , J. Carpenter[1], P. Klenk[1], C. V. Varanasi[3], P. N. Barnes[1]

[1]Air Force Research Laboratory
WPAFB, OH, 45433, USA

[2]University of Houston, Department of Mechanical Engineering
Houston, TX, 77204, USA

[3]University of Dayton Research Institute,
300 College Park, Dayton, OH, 45469, USA

ABSTRACT

Epitaxial $YBa_2Cu_3O_{7-X}$ (YBCO) films were produced on non-buffered (100) single crystal $LaAlO_3$ using the metal organic deposition (MOD) method with fluorinated metal acetates. In an effort to enhance the in-field performance of the films, Sm and Nd acetates were fractionally substituted for Y acetate in a series of precursor solutions to incorporate an array of nanoscale flux pinning centers in the post-annealed films. From measurements taken in the non-optimized films a 50%-150% improvement in critical current density at 77K in fields up to 1T were found for films with a 1/3 substitution of the Rare Earth elements, with further improvements at 40K. Furthermore, a study of the microstructure of the films by scanning electron microscopy (SEM) reveals the presence of nanoparticles on the surfaces of the films.

KEYWORDS: MOD, Metal Organic Deposition, YBCO, Sm, Nd, substitution, Rare Earth
PACS: 74.62.Dh, 74.78.Bz, 74.72.Bk

INTRODUCTION

Second generation high-temperature superconductor (HTS) wire is based on an epitaxial YBCO film grown on a biaxially textured substrate. A primary concern in the development of second-generation HTS wire is choosing a cost-effective manufacturing process that maintains the high electrical performance obtained by laboratory methods.

CP824, *Advances in Cryogenic Engineering: Transactions of the International Cryogenic Materials Conference - ICMC, Vol. 52,* edited by U. Balachandran

This requires the minimization of initial capital investments and ongoing processing costs while maintaining the performance required for practical applications.

The Trifluroacetate-Metal Organic Deposition (TFA-MOD) process is being used in the scale up of coated conductor production, since it provides a low cost solution with the added benefits of high production rate, no vacuum equipment requirements, large scale film uniformity, and high critical current densities[1] . However, in order to be utilized in the full spectrum of power applications, such as generators, transformers, etc... the in-field performance of the HTS films must be enhanced. One method of achieving this enhancement is to incorporate nanoscale defects into the microstructure to act as magnetic flux pinning centers that create a potential barrier to flux flow. Although these defects have been investigated in films produced by Pulsed Laser Deposition (PLD), significantly less has appeared in the literature for MOD derived films[2,3]. Furthermore, techniques used to incorporate nanoparticles in PLD may not transfer over to MOD, due to the differences in the growth mechanisms and processing environments. In this initial report of an investigation to determine the optimal method of enhancing the in-field performance of TFA-MOD YBCO the most straight-forward method of introducing pinning centers into the film is addressed; that of Rare Earth elemental substitution for Y. It was previously demonstrated that that by substituting Yttrium by other RE elements, the in-field properties could be dramatically improved [4,5,6] due to stress field induced flux pinning.

Compared to other deposition methods, it may be simpler to incorporate RE elements for Y substitution using MOD. Only the replacement of a portion of the Y acetate by one or more RE acetates is needed in the preparation of the precursor solution. Furthermore, due to the similar chemical properties of the metal ions and sizes of the superconducting lattice unit cells, substitution does lead to large degradation in the film, but can still produce pinning centers. In this portion of the study the RE elements of Sm and Nd were substituted for Y. The lattice mismatch of the SmBCO and NdBCO unit cells in comparison to YBCO are a= -0.41%, b= -0.34%, c= -0.29% and a= -0.40%, b= -0.34%, c= -0.34%, respectively; thus producing tensile stress when incorporated into a YBCO lattice and possibly leading to phase separation.

EXPERIMENTAL

The YBCO precursor solution was prepared by dissolving amounts of Y, Sm, Nd, Ba, and Cu acetates in TFA according to a stiochiometric ratio of $Y_{1-X}RE_XBa_2Cu_3$ where RE=Sm or Nd and X=⅓, ⅔ or 1. The solution was refluxed for 4 hours and subsequently heated to remove TFA. To remove traces of TFA, water and acetic acid the purifying method suggested by Araki et al. was used [7]. Thus, the resulting gel was dissolved in methanol and refluxed several times at 323K. The purified gel was dissolved in methanol to attain a final solution concentration of 0.25M. The precursor solution was deposited on $LaAlO_3$ <100> substrates. Excess solution was removed by spinning the films at 4000rpm for 120s in air. The samples were heat treated with a schedule similar to the one reported by Y.-A. Jee et al. [8].

Samples where analyzed to determine the texture and microstructure. The texture was analyzed using X-ray difraction and the microstructure was characterized utilizing SEM. A Rigaku coupled 2θ goniometer along with a Phillips Materials Research Diffractometer utilizing CuKα1 radiation were used to obtain 2θ scans. The 2θ scans were taken between 10° and 120° with a step size of 0.05° and a scan rate of 6°/min. The SEM used for surface imaging is a Sirion microscope made by FEI.

RESULTS

Figures 1 and 2 display the X-ray diffraction patterns of $Y_{1-X}Nd_XBa_2Cu_3O_{7-Y}$ and $Y_{1-X}Sm_XBa_2Cu_3O_{7-Y}$ where X= 0, ⅓, ⅔ and 1. Only the (00*l*) peaks appear in the RE substituted films and are located at the same positions as those of YBCO. This shows the successful growth of the substituted textured films and is supported by measured T_{Conset} values of ~92K and transition widths of 2-4K for YBCO and RE substituted samples. The intensity of the peaks decrease with the addition of Nd or Sm, which implies that the crystallinity or unit cell structures are changing with increased dopant concentration. It must be noted that these films were processed using parameters developed for YBCO. They are therefore not optimized and it is possible that under different conditions less change would be observed. In particular use of a higher temperature during the conversion process might provide a significant improvement in crystallinity; since NdBCO and SmBCO both have a higher formation temperature than YBCO.

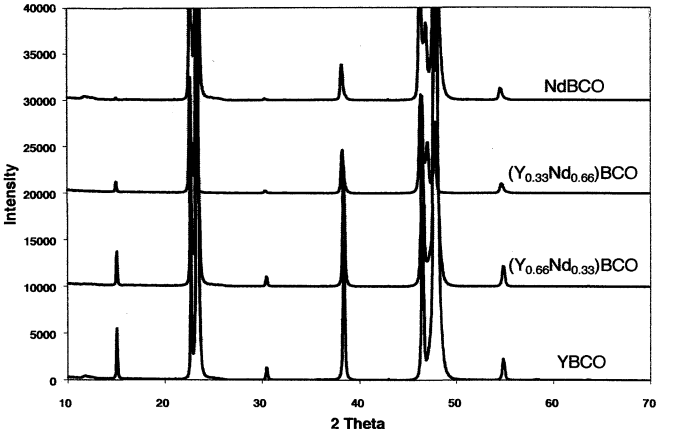

FIGURE 1. X-ray diffraction patterns for $Y_{1-X}Nd_XBa_2Cu_3O_{7-Y}$ where X= 0, ⅓, ⅔ and 1.

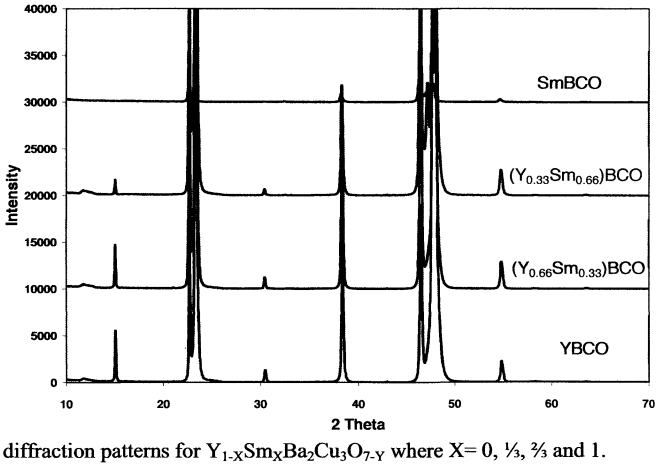

FIGURE 2. X-ray diffraction patterns for $Y_{1-X}Sm_XBa_2Cu_3O_{7-Y}$ where X= 0, ⅓, ⅔ and 1.

Figures 3 and 4 display the in-field critical current density of several Sm and Nd doped films compared to YBCO at 77K and 40K, respectively. The in-field critical current is significantly improved by the ⅓ substitutions of Sm and Nd. At 77K in fields up to 1T 50%-150% improvements in critical current density were found for these films. While the $Sm_{0.33}$ curve remains nearly constant in relation to YBCO at 40K, the $Nd_{0.33}$ curve exhibits a further improvement in performance. At 40K the $Nd_{0.33}$ film has a critical current density ≥100% larger than YBCO up to 4T, ≥50% larger up to 8T and some level of improvement up to 10T. Only the $Sm_{0.66}$ sample shows deterioration in the film quality. At 77K the entire curve of J_C is below that of YBCO and shows such a large negative slope that at 1.5T J_C is only 15% of the YBCO value. At 40K there is some improvement at fields less than 4.5T, however at that field density there is a crossover and the performance is degraded at higher fields. These results call for a more detailed investigation of substitutions around 33% and lower concentrations in order to determine an optimal doping level.

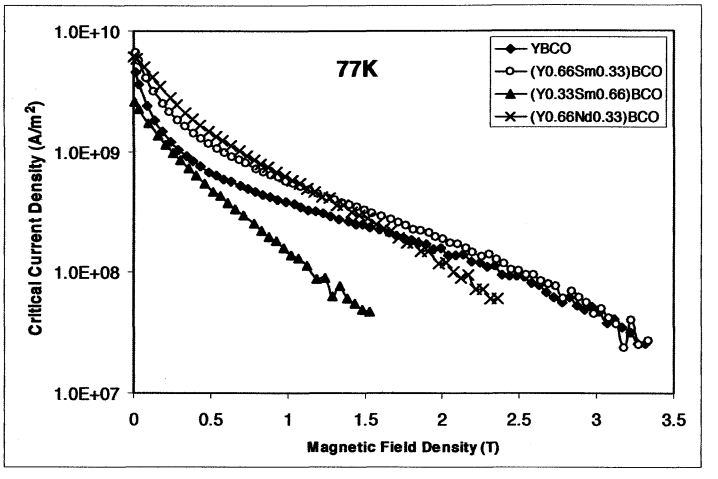

FIGURE 3. In-field critical current density of films at 77K.

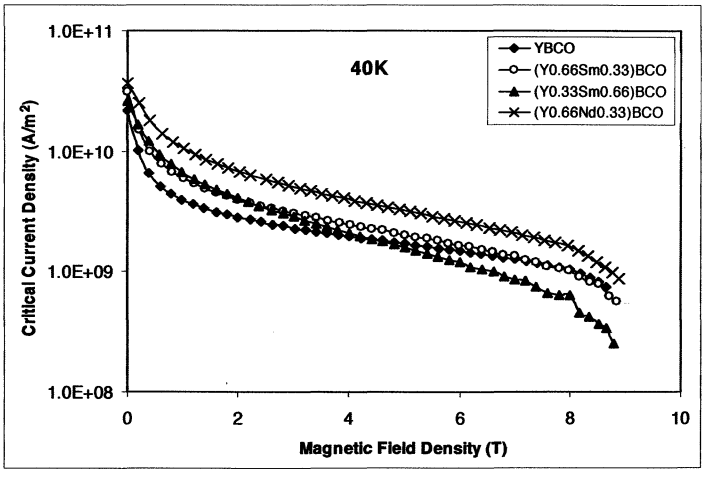

FIGURE 4. In-field critical current density of films at 40K.

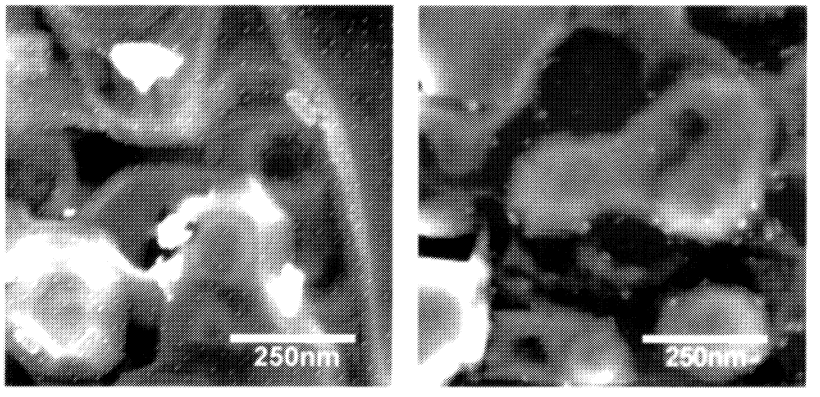

FIGURE 5. SEM pictures of the $Y_{0.66}Nd_{0.33}Ba_2Cu_3O_{7-Y}$ (left) and $Y_{0.66}Sm_{0.33}Ba_2Cu_3O_{7-Y}$ (right).

SEM images of the $Y_{0.66}Nd_{0.33}Ba_2Cu_3O_{7-Y}$ and $Y_{0.66}Sm_{0.33}Ba_2Cu_3O_{7-Y}$ films are shown in Figure 5. Nanoparticles less than 10nm wide are present on both of the substituted films. These particles are not observed on pure YBCO film. On the $Nd_{0.33}$ film the particles are randomly, uniformly arrayed, while on the $Sm_{0.33}$ film, the nanoparticles decorate the grain boundaries. Although a cross-sectional TEM analysis would be needed to confirm the presence of nanoparticles inside the films, the surface particles suggests that phase separation has occurred for both RE substitutions.

CONCLUSIONS

This initial report of a study on the optimization of in-field properties of second generation HTS wire produced by MOD reveals a significant improvement of the critical current density of YBCO films by the fractional substitution of the RE elements Nd and Sm for Y. Additionally, the nanoparticles on the surface of the films suggest that the improvement may be due to the presence of particulate pinning centers within the films brought about by phase separation. In higher quality films these nanoparticles are anticipated to likewise improve the in-field performance; however, in order to verify these results the baseline YBCO film quality must be further improved and the proper processing parameters determined for the substituted films.

REFERENCES

1. A. P. Malozemoff, "Second Generation HTS Wire: *An Assessment*", American Superconductor White Paper, July (2004)
2. A. Kaneko, J. Matsuda, R. Teranishi, K. Nakaoka, Y. Aoki, H. Fuji, K. Murata, T. Goto, A. Yoshinaka, A. Yajima, T. Izumi, Y. Shiohara, *Physica C*, **426-431**, pp. 949-953 (2005)
3. U. Schoop, M. W. Rupich, C. Thieme, D. T. Verebelyi, W. Zhang, X. Li, T. Kodenkandath, N. Nguyen, E. Siegal, L. Civale, T. Holesinger, B. Maiorov, A. Goyal, P. Paranthaman, *IEEE Trans. Appl. Supercoduc.*, **15**, pp. 2611-2616 (2005)
4. C. Cai, B. Holzapfel, J. Hanisch, L. Fernandez, L. Schultz, *Phys. Rev. B*, **69**, pp. 104531-104534 (2004).
5. J. L. MacManus-Driscoll, S. R. Foltyn, Q. X. Jia, H. Wang, A. Serquis, B. Maiorov, L. Civale, Y. Lin, M. E. Hawley, M. P. Maley, D. E. Peterson, *Appl. Phys. Lett.*, **84**, pp. 5329-5331 (2004)
6. J. W. Kell, T. J. Haugan, M. F. Locke, P. N. Barnes, *IEEE Trans. Appl. Supercoduc.*, **15**, pp. 3726-3729 (2005)

7. T. Araki, I. Hirabayashi, Supercond. Sci. Technol., **16**, pp. 7-11 (2001).
8. Y.-A. Jee, M.Li, B. Ma, V. A. Maroni, B. L. Fisher, U. Balachandran, *Physica C*, **356**, pp. 297-303 (2001).